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(54) Process for preparing high bulk density detergent powders containing clay.

(57) A process for preparing a granular detergent composition or component having a bulk density of at least 550 g/l, which comprises the steps of adding up to 35% by weight of a swelling clay to a particulate starting material comprising:

(a) from 10 to 70% by weight of non-soap detergent active material, and

(b) at least 10% by weight of water-soluble crystalline inorganic salts, including sodium tripolyphosphate and/or sodium carbonate,

the weight ratio of (a) to (b) being at most 2.5, and treating the mixture in a high-speed mixer/granulator having both a stirring action and a cutting action. The obtained granular detergent composition has good powder dissolution properties, a good softening in the wash performance and a good storage stability.

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PROCESS FOR PREPARING HIGH BULK DENSITY DETERGENT POWDERS CONTAINING CLAY

TECHNICAL FIELD

The present invention relates to a process for preparing a granular detergent composition or component having a high bulk density and good powder properties. More in particular, it relates to a process for the preparation of a granular detergent composition having good powder dissolution properties and a good softening in the wash performance.

BACKGROUND AND PRIOR ART

Recently there has been considerable interest within the detergents industry in the production of detergent powders having a relatively high bulk density, for example 550 g/l and above.

Generally speaking, there are two main types of processes by which detergent powders can be prepared. The first type of process involves spray-drying an aqueous detergent slurry in a spray-drying tower. In the second type of process, the various components are dry-mixed and optionally agglomerated with liquids, e.g. nonionics.

The most important factor that governs the bulk density of a detergent powder is the bulk density of the starting materials in the case of a dry-mixing process, or the chemical composition of the slurry in the case of a spray-drying process. Both factors can only be varied within a limited range. For example, the bulk density of a dry-mixed powder can be increased by increasing its content of relatively dense sodium sulphate, but the latter does not contribute to the detergency of the powder, so that its overall properties as a washing powder will generally be adversely affected.

Therefore, a substantial increase in bulk density can only be achieved by additional processing steps which lead to densification of the detergent powders. There are several processes known in the art leading to such densification. Particular attention has thereby been paid to the densification of spray-dried powders by post-tower treatment.

For instance, the Japanese patent application 61 069897 (Kao) discloses a process in which a spray-dried detergent powder containing a high level of anionic surfactant and a low level of builder (zeolite) is subjected successively to a pulverizing and a granulating treatment in a high-speed mixer/granulator. The granulation is carried out in the presence of an "agent for improving surface properties" and optionally a binder.

It is also known to incorporate smectite clays into detergent powders for obtaining a fabric-softening effect. Furthermore, the British patent specification 2,063,289 (Unilever) discloses that detergent powders containing less than 20% by weight of a phosphate salt and more than 20% by weight of anionic surfactant may be rendered crisp and free-flowing by addition of 1-15% of bentonite or kaolin to the crutcher slurry.

One of the inherent problems of detergent compositions having a high bulk density is, however, that their dissolving behaviour is usually reduced relative to a corresponding composition having a lower bulk density. This may be attributed to the lower particle porosity of the powder.

We have now surprisingly found that the admixture of a swelling clay to a particulate detergent starting material followed by treating the mixture in a high-speed mixer/granulator having both a stirring action and a cutting action provides a high bulk density detergent powder having much better dissolution properties and softening properties than when the clay is admixed to the crutcher slurry followed by spray-drying.

DEFINITION OF THE INVENTION

In a first aspect, the present invention provides a process for the preparation of a granular detergent composition or component having a bulk density of at least 550 g/l, which comprises the steps of adding up to 35% by weight of a swelling clay to a particulate starting material comprising:

(a) from 10 to 70% by weight of non-soap detergent active material, and

(b) at least 10% by weight of water-soluble crystalline inorganic salts, including sodium tripolyphosphate and/or sodium carbonate,

the weight ratio of (a) to (b) being at most 2.5, and treating the mixture in a high-speed mixer/granulator having both a stirring action and a cutting action.

DETAILED DESCRIPTION OF THE INVENTION

In the process of the present invention, a particulate starting material is admixed with a swelling clay and treated in a high-speed mixer/granulator.

The starting material for th process according to th invention comprises (a) from 10 to 70% by weight of non-soap detergent active material, and (b) at least 15% by weight of water-solubl crystalline inorganic salts, including sodium tripolyphosphate and/or sodium carbonate, the weight ratio of

(a) to (b) being at most 2.5. Preferably the ratio of (a) to

(b) is from 0.1 to 2.0, even more preferably from 0.1 to 0.4.

The starting material comprises the compounds usually found in detergent compositions such as detergent active materials, builders, and so forth, all well known in the art.

The detergent active material may be selected from non-soap anionic, ampholytic, zwitterionic or nonionic detergent active materials or mixtures thereof. Particularly preferred are all anionic or mixtures with nonionic detergent active materials such as a mixture of an alkali metal salt of an alkyl benzene sulphonate together with an alkoxylated alcohol.

The preferred detergent compounds which can be used are synthetic anionic and nonionic compounds. The former are usually water-soluble alkali metal salts of organic sulphates and sulphonates having alkyl radicals containing from about 8 to about 22 carbon atoms, the term alkyl being used to include the alkyl portion of higher acyl radicals. Examples of suitable synthetic anionic detergent compounds are sodium and potassium alkyl sulphates, especially those obtained by sulphating higher (C_8-C_{18}) alcohols, produced for example from tallow or coconut oil, sodium and potassium alkyl (C_9-C_{20}) benzene sulphonates, particularly sodium linear secondary alkyl (C_{10}-C_{15}) benzene sulphonates; sodium alkyl glyceryl ether sulphates, especially those ethers of the higher alcohols derived from tallow or coconut oil and synthetic alcohols derived from petroleum; sodium coconut oil fatty monoglyceride sulphates and sulphonates; sodium and potassium salts of sulphuric acid esters of higher (C_8-C_{18}) fatty alcohol-alkylene oxide, particularly ethylene oxide, reaction products; the reaction products of fatty acids such as coconut fatty acids esterified with isethionic acid and neutralized with sodium hydroxide; sodium and potassium salts of fatty acid amides of methyl taurine; alkane monosulphonates such as those derived by reacting alpha-olefins (C_8-C_{20}) with sodium bisulphite and those derived from reacting paraffins with SO_2 and Cl_2 and then hydrolysing with a base to produce a random sulphonate; and olefin sulphonates, which term is used to describe the material made by reacting olefins, particularly C_{10}-C_{20} alpha-olefins, with SO_3 and then neutralizing and hydrolysing the reaction product. The preferred anionic detergent compounds are sodium (C_{11}-C_{15}) alkyl benzene sulphonates and sodium (C_{16}-C_{18}) alkyl sulphates.

Suitable nonionic detergent compounds which may be used include, in particular, the reaction products of compounds having a hydrophobic group and a reactive hydrogen atom, for example, aliphatic alcohols, acids, amides or alkyl phenols with alkylene oxides, especially ethylene oxide either alone or with propylene oxide. Specific nonionic detergent coompounds are alkyl (C_6-C_{22}) phenols-ethylene oxide condensates, generally 5 to 25 EO, i.e. 5 to 25 units of ethylene oxide per molecule, the condensation products of aliphatic (C_8-C_{18}) primary or secondary linear or branched alcohols with ethylene oxide, generally 5 to 40 EO, and products made by condensation of ethylene oxide with the reaction products of propylene oxide and ethylenediamine. Other so-called nonionic detergent compounds include long-chain tertiary amine oxides, long-chain tertiary phosphine oxides and dialkyl sulphoxides.

Mixtures of detergent compounds, for example, mixed anionic or mixed anionic and nonionic compounds, may be used in the detergent compositions, particularly in the latter case to provide controlled low sudsing properties. This is beneficial for compositions intended for use in suds-intolerant automatic washing machines.

Amounts of amphoteric or zwitterionic detergent compounds can also be used in the compositions of the invention but this in not normally desired owing to their relatively high cost. If any amphoteric or zwitterionic detergent compounds are used, it is generally in small amounts in compositions based on the much more commonly used synthetic anionic and/or nonionic detergent compounds.

The detergency builder may be any material capable of reducing the level of free calcium ions in the wash liquor and will preferably provide the composition with other beneficial properties such as the generation of an alkaline pH, the suspension of soil removed from the fabric and the suspension of the fabric-softening clay material. The level of the detergency builder may be from 10% to 70% by weight, most preferably from 25% to 50% by weight.

Examples of detergency builders include precipitating builders such as the alkali metal carbonates, bicarbonates, orthophosphates, sequestering builders such as the alkali metal tripolyphosphates or nitrilotriacetates, or ion exchange builders such as th amorphous alkali metal aluminosilicat s or th zeolites.

The starting material may be prepared by any suitable method, such as spray-drying or dry mixing. A

suitable particulate material may also be prepared by a dry n utralization process in which a liquid acid anionic surfactant precursor is reacted with a solid alkaline inorganic component, such as carbonate. Such dry neutralization processes are for example disclosed in the British Patents 2 166 452 (Kao), 1 404 317 (Bell) or 1 369 269 (Colgate).

In the process of the invention, the starting material is fed into a high-speed mixer/granulator having both a stirring action and a cutting action. The preferred type of high-speed mixer/granulator for use in the process of the invention is bowl-shaped and has a substantially vertical stirrer axis. It is especially preferred when the mixer/granulator additionally has cutter means positioned on a side wall. These stirrer and cutter means may advantageously be operated independently of one another, and at separately variable speeds. It is also preferred if the vessel of the mixer is equipped with a jacket for cooling or heating purposes. If necessary, cooling may be effected by means of a cryogenic unit.

Examples of preferred mixers are the Fukae (Trade Mark) FS-G series manufactured by Fukae Powtech Kogyo Co., Japan, e.g. the Fukae FS30. This apparatus is essentially in the form of a bowl-shaped vessel accessible via a top port, provided near its base with a stirrer having a substantially vertical axis, and a cutter on a side wall.

A similar mixer manufactured in India is the Sapphire (Trade Mark) RMG series of rapid mixer/granulators, which, like the Fukae mixer, is available in a range of different sizes. This apparatus is essentially in the form of a bowl-shaped vessel raised up pneumatically to seal against a fixed lid. A three-bladed stirrer and a four-bladed shutter share a single substantially vertical axis of rotation mounted on the lid. The stirrer and cutter may be operated independently of one another, the stirrer at speeds of 75 rpm or 150 rpm, and the cutter at speeds of 1440 rpm or 2880 rpm. The vessel can be fitted with a water jacket which may be used to cool or heat the content of the vessel.

The Sapphire RMG-100 mixer, which is suitable for handling a 60 kg batch of detergent powder, has a bowl of about 1 meter diameter and 0.3 meters deep; the working capacity is 200 liters. The stirrer blades are of 1 meter diameter and the cutter blades are of 0.1 meter diameter.

Other similar mixers found to be suitable for use in the process of the invention include the Diosna (Trade Mark) V series ex Dierks and Söhne, Germany; and the Pharma Matrix (Trade Mark) ex T.K. Fielder Ltd, England. Other mixers believed to be suitable for use in the process of the invention are the Fuji (Trade Mark) VG-C series ex Fuji Sangyo Co., Japan; and the Roto (Trade Mark) ex Zanchetta & Co. srl, Italy.

Yet another mixer found to be suitable for use in the process of the invention is the Lodige (Trade Mark) FM series batch mixer ex Morton Machine Co. Ltd, Scotland. This differs from the mixers mentioned above in that its stirrer has a horizontal axis.

These apparatus (which may be continuous or batch fed) essentially consist of a large, static hollow cylinder and a rotating shaft in the middle. The shaft has several different types of blades mounted thereon. The rotation speed, which may be variable, will depend on the degree of densification and the particle size desired. The blades on the shaft provide a thorough mixing action of the solids and the liquids which may be admixed at this stage. The mean residence time is somewhat dependent on the rotational speed of the shaft and the position of the blades with continuous plant. High-speed cutter blades, independently driven, may also be incorporated in this type of mixer operating normally to the main agitator, e.g. Lodige (Trade Mark) KM series or Drais (Trade Mark) KT series.

The use of the high-speed mixer/granulator is essential to obtain granulation and densification. Before the granulation of the starting material takes place, a pretreatment may be carried out, for example a pulverization step. Whether this is necessary is dependent, amongst other things, on the method of preparing of the starting material, its particle size and moisture content. For example, spray-dried powders are more likely to require a pulverization pretreatment than dry-mixed powders. In order to carry out the pulverization a suitable stirring/cutting regime must be chosen which will generally be characterized by relatively high speeds for both the stirrer and the cutter and a relatively short residence time, for example of 1 to 4 minutes.

The granulation step is similarly carried out by running the stirrer and the cutter at a relatively high speed, but here the presence of a liquid binder is necessary. The preferred binder is water. The amount of binder added should preferably not exceed about 6 % by weight, because higher levels may adversely affect the flow properties of the final product. The liquid binder may be added before or during granulation, preferably by spraying it in while the apparatus is running. The starting material may also already contain sufficient moisture, such that addition of further liquid binder is not necessary. In this case, pulverizati n and granulation may be carried out as a single operation.

According to a preferred embodiment of the invention, the granulation is carried out at a temperatur above ambient, such as a temperature above 30 or 45 °C. For example, a spray-dried detergent base powder leaving the tower at a temperature of approximately 45°C or above may be fed directly into the

process of the present invention. Of course, the spray-dried powder may be cooled first, e.g. by means of an airlift.

In the process of the present inv ntion, a swelling clay is added to the mixer/granulator in an amount of up to 35% by weight of the starting material. The swelling clay material may be any such material capable of providing a fabric-softening benefit. Usually these materials will be of natural origin containing a three-layer swellable smectite clay. Preferably, the clay is of the calcium and/or sodium montmorillonite type.

The effectiveness of a clay-containing material as a fabric softener will depend amongst other things on the level of smectite clay. Impurities such as calcite, feldspar and silica will often be present. Relatively impure clays can be used, provided that such impurities are tolerable in the composition.

The level of the fabric-softening clay material in the composition should be sufficient to provide a softening benefit. Amounts from 1.5% to 35% by weight, preferably from 4% to 20% by weight, calculated on the basis of the clay mineral per se were found to be effective.

In addition to the detergent active material, the detergency builder and the clay-containing material, the compositions according to the invention optionally may contain other ingredients usually found in detergent compositions, in the amounts in which such additives are normally employed in fabric-washing detergent compositions. Examples of such additives include the lather boosters such as alkanolamides, particularly the monoethanolamides derived from palm kernel fatty acids and coconut fatty acids, lather depressants, oxygen releasing bleaching agents such as sodium perborate and sodium percarbonate, peracid bleach precursors, chlorine releasing bleaching agents such as trichloroisocyanuric acid, fillers such as sodium sulphate, and, usually present in very minor amounts, fluorescent agents, perfumes, enzymes such as proteases, lipases and amylases, germicides and colorants.

The process of the present invention enables the preparation of detergent compositions having a high bulk density of at least 550 g/l. It is a surprising advantage of the process of the invention that the bulk density of the obtained powders is higher than when the clay is admixed to the crutcher slurry prior to spray-drying of the starting material.

A further advantage of the process of the invention is that the softening action of the final detergent powder is improved relative to when the clay is admixed to the crutcher slurry followed by spray-drying. This effect of the present process can be established by methods used for assessment of softening delivery as they have previously been described in the art.

It is a further advantage of the process of the present invention that the storage stability of the final detergent powder is improved. This can be established by means of the Unconfined Compressibility Test (UCT). In this test the detergent powder is placed in a cylinder having a diameter of 13 cm and a height of 15 cm. Subsequently, a weight of 10 kg is placed on top of the powder. After 5 minutes the weight is removed and the walls of the cylinder are taken away. Then an increasing load is placed on top of the column of compressed detergent powder and the weight (in kg) is determined at which the column disintegrates. This value is a function of the stickiness of the detergent powder and proved to be a good measure for the storage stability.

The invention will now be further illustrated by the following non-limiting examples, in which parts and percentages are by weight unless otherwise indicated.

In the Examples which follow, the following abbreviations are used for the materials employed:

LAS	: Linear alkyl benzene sulphonate
STP	: Sodium tripolyphosphate
Silicate	: Sodium alkaline silicate
Carbonate	: Sodium carbonate
Sulphate	: Sodium sulphate
Clay	: Calcium or sodium montmorillonite

EXAMPLES 1-3

The following detergent powders were prepared by spray-drying aqueous slurries. The compositions (in % by weight) of the powders thus obtained are given below.

TABLE 1

Example	1	2	3
LAS	31	34	34
total NSD (a)	31	34	34
STP	41	46	46
Silicate	5	6	6
Carbonate	8	-	9
Sulphate	10	-	-
total Salts (b)	64	52	61
Clay	-	10	-
Water	5	4	5
Ratio (a):(b)	0.48	0.65	0.56

The composition of Example 2 contained a Ca-clay (Prassa ex Colin Stewart Minerals, U.K.) which was added to the crutcher slurry and spray-dried. Sodium carbonate was in this case omitted from the slurry to maintain it at a sufficiently low viscosity to aid in spray-drying. Example 3 was a spray-dried powder without clay but including carbonate.

The compositions of Examples 2 and 3 had a higher percentage by weight of LAS, STP and silicate than the composition of Example 1 to allow for dilution on post-dosing of either carbonate or clay, respectively, during the densification/ granulation step.

The powders were added (10 kg - Example 1; 9.2 kg - Example 2; 9.0 kg - Example 3) to a Fukae FS-30 high-speed mixer/ granulator. The powders were pulverized for 2 minutes at 70°C with a stirrer rotation of 300 rpm and a cutter rotation of 3000 rpm. Subsequently, 0.8 kg sodium carbonate and 1.0 kg Ca-clay were added to the densified powders of Examples 2 and 3. Granulation was then effected by addition of about 150 ml water over a time period of one minute at a stirrer rotation speed of 275 rpm and a cutter rotation speed of 3000 rpm. The resulting powders were sieved for oversize (>1700 μm). The composition (in % by weight) of the powders was as follows:

TABLE 2

Examples	1	2	3
LAS	31	31	31
STP	41	41	41
Silicate	5	5	5
Carbonate	8	8	8
Clay	-	10	10
Sulphate	10	-	-
Water	5	5	5

The powder properties of the sieved materials are given below in Table 3.

TABLE 3

Examples	1	2	3
Bulk Density (g/l)	965	738	980
Dynamic Flow Rate (cm^3/s)	149	145	150
UCT	2.9	8.2	2.9
Particle Size (μm)	870	699	856
N	2.33	1.45	2.70

wherein UCT is % unconfined compressibility and N is the distribution of mean particle size.

The dissolution properties of the concentrated powders described in Tables 2 and 3 and the respective undensified control powders were measured by standard conductometric techniques. A sieved fraction of the powder samples (-500 + 425 μm) was used to ensure that the dissolution behaviour of a comparable particle size range was compared. In order to compensate for inevitable differences in powder properties such as bulk density, etc., the rate of dissolution was compared to the ratio SA_g/SA_b where SA is the surface area per unit weight of a given granulated powder (g) or undensified base (b). The ratio SA_g/SA_b therefore represents a scale of concentration. The surface area per kg (SA) for a specific powder was calculated (assuming spherical particles) from the formula:

$SA = 6 /(BD \times d_m)$

where BD stands for bulk density and d_m for mean diameter (μm).

The results of the dissolution experiments are given in Table 4 and are graphically shown in Figure 1. In the Figure, a linear relationship is observed between the dissolution rate and the ratio SA_g/SA_b for the concentrated powders from Examples 1 and 2 and the unconcentrated base powder of Example 1. This indicates that the dissolution rate is a function of the surface area available for mass transfer. The Figure shows for Example 3, whereby the clay was post-dosed prior to granulation, that the dissolution rate is higher than expected for a comparable powder. This illustrates that the clay is contributing to improved dissolution properties

TABLE 4

Examples	1	2	3
Dissolution Rate (s^{-1})	1.92	2.54	2.85
SA_g/SA_b	0.23	0.47	0.31
% Softness	0	75.3	99.5

Also shown in Table 4 are the softening properties of the various compositions. The softening delivery of concentrated powders of Examples 1-3 was measured on terry toweling fabric. Tergotometer washes at a powder concentration of 3.6 g/l were performed for 30 minutes with a cloth to liquor weight ratio of 1:20. The relative softening delivery was measured according to standard practice by a trained panel of ten people, as described in the art.

The superior softening delivery of the composition of Example 3 according to the invention (in which the clay was post-dosed during granulation) may also be illustrated by a further comparative experiment whereby the clay powder was added to Example 1 during the wash at concentrations equivalent to Example 3.

When the clay was added separately to the wash using the composition of Example 1, a softness value of 97.5 was found. Comparison of this value with the softness value of 99.5 found for Example 3 indicates that essentially the full softening performance is delivered by the process of the invention. However, when the clay was added to th crutcher slurry prior to spray-drying as in Example 2, a much lower softness value of 75.3 was found.

Claims

1. Process for the preparation of a granular detergent composition or component having a bulk density of at least 550 g/l, which comprises th steps of adding up to 35% by weight of a swelling clay to a particulate starting material comprising:
   (a) from 10 to 70% by weight of non-soap detergent active material, and
   (b) at least 10% by weight of water-soluble crystalline inorganic salts, including sodium tripolyphosphate and/or sodium carbonate,
   the weight ratio of (a) to (b) being at most 2.5, and treating the mixture in a high-speed mixer/granulator having both a stirring action and a cutting action.

2. Process according to Claim 1, wherein the ratio of (a) to (b) is from 0.1 to 2.0, and preferably from 0.1 to 1.0.

3. Process according to any one of the preceding Claims, wherein the swelling clay is a calcium and/or sodium montmorillonite type clay.

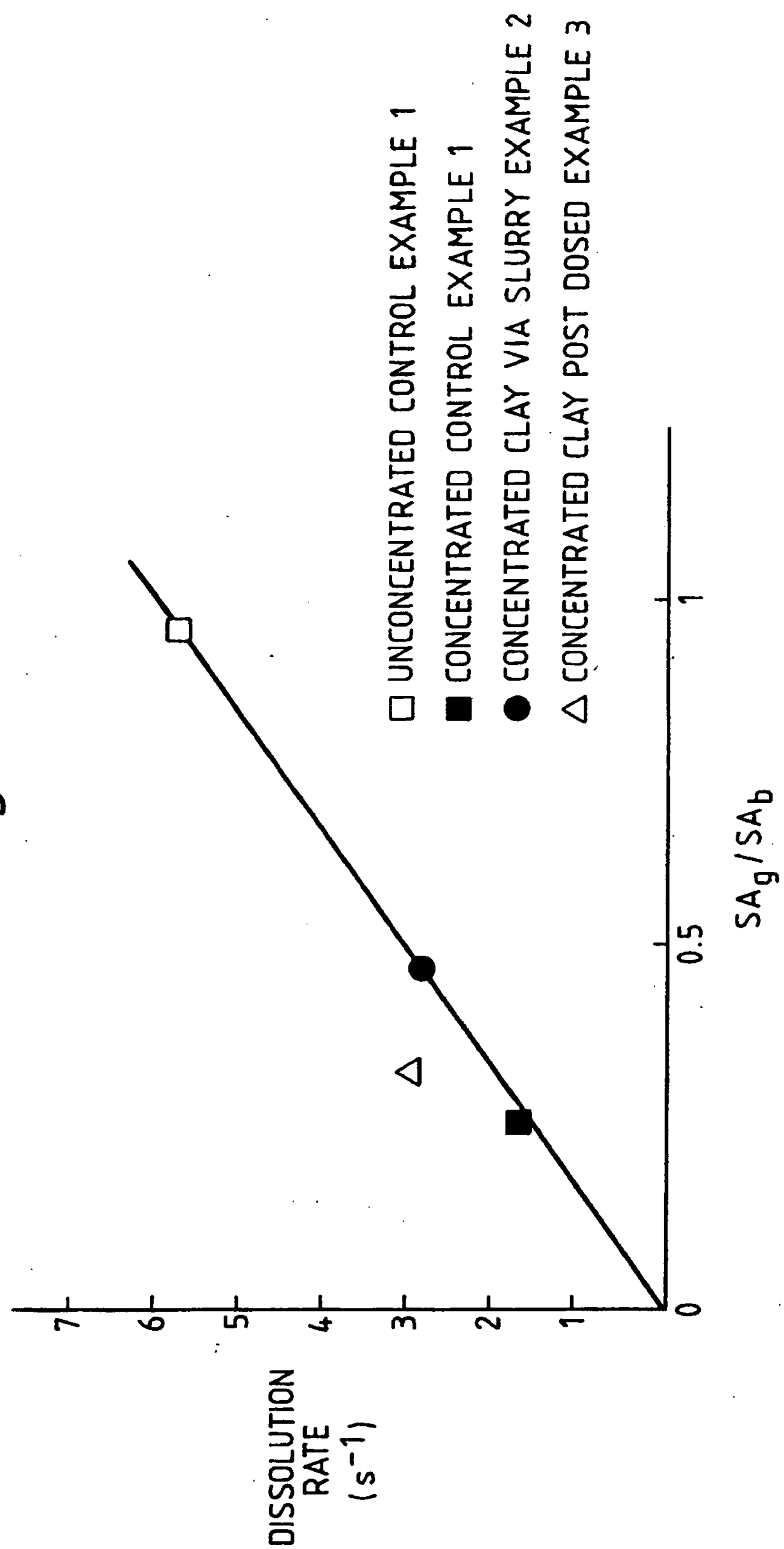
4. Process according to any one of the preceding Claims, wherein the mixer/granulator is a bowl-type high-speed mixer/ granulator having a substantially vertical stirrer axis.

5. Process according to any one of the preceding Claims, wherein the particulate starting material comprises spray-dried detergent powder.

6. Process according to any one of the preceding Claims, wherein the particulate starting material comprises from 15 to 50 % by weight sodium tripolyphosphate.

7. Process according to any one of the preceding Claims, wherein the granulation is carried out at a temperature of at least 45 °C.

Fig. 1.


DISSOLUTION
RATE
(s^{-1})
7
6
5
4
3
2
1
0
0.5
1
SA_g/SA_b
□ UNCONCENTRATED CONTROL EXAMPLE 1
■ CONCENTRATED CONTROL EXAMPLE 1
● CONCENTRATED CLAY VIA SLURRY EXAMPLE 2
△ CONCENTRATED CLAY POST DOSED EXAMPLE 3